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WATER PROGRAM

Benzidine: Proposed Toxic Pollutant Effluent Standards

ENVIRONMENTAL PROTECTION AGENCY

[40 CFR Part 129]

[FRL 564-4]

WATER PROGRAM

Benzidine; Proposed Toxic Pollutant Effluent Standards

Notice is hereby given that the Environmental Protection Agency, pursuant to the authority contained in section 307(a) of the Federal Water Pollution Control Act (the Act) as amended by the Federal Water Pollution Control Act Amendments of 1972 (Pub. L. 92-500, 86 Stat. 816, (33 U.S.C. 1251 *et seq.*)), proposes additional sections to Part 129, setting forth proposed effluent standards for benzidine. On June 10, 1976, the Agency proposed a new Part 129, setting forth proposed effluent standards for the following toxic pollutants: aldrin/dieldrin, DDT (DDD, DDE), endrine and toxaphene, 41 FR 23576. Those four pollutants, as well as benzidine, were included on a list of toxic pollutants previously published by the Agency pursuant to section 307(a)(1), 38 FR 24342 *et seq.* (September 7, 1973).

Section 307(a)(2) of the Act provides as follows:

> Within one hundred and eighty days after the date of publication of any list, or revision thereof, containing toxic pollutants or combination of pollutants under paragraph (1) of this subsection, the Administrator, in accordance with section 553 of title 5 of the United States Code, shall publish a proposed effluent standard (or prohibition) for such pollutant or combination of pollutants which shall take into account the toxicity of the pollutant, its persistence, degradability, the usual or potential presence of the affected organisms in any waters,t he importance of the affected organisms and the nature and extent oft he effect of the toxic pollutant on such organisms, and he shall publish a notice for a public hearing on such proposed standard to be held within thirty days. As soon as possible after such hearing, but not later than six months after publication of the proposed effluent standard (or prohibition), unless the Administrator finds, on the record, that a modification of such proposed standard (or prohibition) is justified based upon a preponderance of evidence adduced at such hearings, such standard (or prohibition) shall be promulgated.

The regulations proposed at this time establish effluent standards for benzidine-based dye manufacturers, and manufacturers of paper goods, leather goods and textile goods who utilize benzidine-based dyes in their production or processes. Standards are proposed for both existing and new sources.

The following, together with the materials and information hereinafter referred to and incorporated by reference, sets forth the statement of basis and purpose of the effluent standards proposed at this time.

Summary of Principal Features and Benefits of the Proposed Regulations

The regulations herein proposed would establish effluent standards for all manufacturers of benzidine and benzidine-based dyes and the principal applicators, or users, of benzidine-based dyes, who discharge directly into the navigable waters. Standards are established for both existing and new sources. Owners and operators of facilities which discharge into publicly owned treatment works, as defined in section 212 of the Act (sometimes referred to as "indirect dischargers"), are not covered by the standards herein proposed. However, the Agency expects to propose pretreatment standards for such indirect dischargers pursuant to the authority contained in section 307 of the Act in due course.

At the present time the Agency has identified three manufacturers of benzidine and benzidine-based dyes. These are Allied Chemical Co., GAF Corp., and Fabricolor, Inc. There are, in addition, numerous facilities which utilize benzidine-based dyes in their operations. The total market for benzidine dyes in 1973 was approximately 30 million pounds. Of this total market approximately 40 percent of the volume was consumed in the manufacture of paper, 25 percent was consumed by the textile industry, 15 percent was used in connection with the production of leather goods, and the remaining 20 percent was scattered among various other industries. Two of the three benzidine-based dye manufacturers presently discharge into publicly owned treatment works and the third, GAF Corp., will do so as soon as the treatment plant is completed. Thus, GAF is presently the only known manufacturer with a direct discharge.

The manufacturers of paper goods, leather goods, and textile goods are divided between facilities with direct discharges into the navigable waters and those with indirect discharges into publicly owned treatment works. Thus, the regulations proposed today, coupled with the pretreatment standards referenced above, will result in coverage of all existing and new benzidine and benzidine-based dye manufacturing sources, and approximately 80 percent of the known benzidine-based dye applicators.

Benzidine is an organic reagent utilized in the synthesis of dyestuffs and also for clinical dyes. It is a proven carcinogen, primarily inducing cancer to the bladder in humans. Historically, the principal exposure route to humans has been through occupational exposure. However, numerous facilities discharge effluents containing benzidine, thus producing the potential for exposure of human beings through direct contact or eventual ingestion of water which may have become contaminated as a result of such discharges. These facts warrant the establishment of standards under section 307 (a) to assure protection of human health and protection for aquatic organisms and others in the food chain.

The proposed standards would establish a maximum allowable direct discharge for any existing or new manufacturer of benzidine or benzidine-based dyes of 0.130 kg benzidine per 1000 kg (kg/kkg) of benzidine produced, calculated on a monthly average. In addition, the average daily concentration of benzidine in discharges calculated over any calendar month may not exceed 10 micrograms per liter ($\mu g/l$), and may at no time exceed 50 $\mu g/l$ in a sample representing any working day. For manufacturers of textile, leather, and paper goods utilizing benzidine-based dye in their processes, the proposed standards would impose a maximum average daily concentration calculated over any calendar month of 10 $\mu g/l$, and a maximum concentration at any time of 25 $\mu g/l$ based on samples or calculations representing any working day. Data available to the Agency indicate that these standards will provide the degree of protection for aquatic and other organisms and human health required by the Act, and are technologically achievable by industry without adverse economic impact.

Few data exist at the present time with respect to the degradation products of benzidine and the toxicity thereof. If such information becomes available which would warrant more stringent standards than those proposed at this time, the Agency will revise any standards promulgated hereunder to provide the appropriate protection pursuant to its authority under section 307(a)(3), which requires that such standards be "reviewed and, if appropriate, revised at least every three years."

I. Background

On July 6, 1973, the Agency published in the Federal Register a proposed list of nine toxic pollutants pursuant to section 307(a)(1) of the Act, 38 FR 18044. The nine substances were aldrin/dieldrin, benzidine, cadmium, cyanide, DDT (DDD, DDE), endrin, mercury, polychlorinated biphenyls, and toxaphene. Following receipt of public comment, the list was promulgated on September 7, 1973, together with a discussion of the Agency's selection criteria and a response to comments received on the proposed list, 38 FR 24342 *et seq.* The promulgated list consisted of the same nine substances previously proposed.

On December 27, 1973, the Agency proposed toxic pollutant effluent standards for each of these nine substances, together with a summary of the factors considered in setting the standards, and a list of point source categories of dischargers proposed for coverage, 38 FR 35388 *et seq.* In accordance with section 307(a)(2) of the Act, a formal rulemaking hearing on the proposed standards was scheduled. A prehearing conference was held on January 25, 1974, followed by a thirty-day evidentiary hearing held during April and May. At the conclusion of those hearings, which were held under severe time constraints, the Agency became aware of problems in the proposed hydrological definitions and of certain gaps in the data base. As a result, the Agency determined at the conclusion of the hearings that the record did not contain sufficient evidence on which to promulgate responsible and defensible standards for any of the substances. Accordingly, the Agency decided to gather additional data and repropose standards, supported by an expanded data base. The present proposed rulemaking therefore

supersedes the proposal of December 27, 1973.

The Agency's decision to gather additional data and to repropose standards was discussed at considerable length in the preamble to the Notice of Proposed Toxic Pollutant Effluent Standards for aldrin/dieldrin, DDT, endrin, and toxaphene, published in the FEDERAL REGISTER on June 10, 1976, 41 FR 23576 to which the reader is referred and which is hereby incorporated by reference.

II. THE PROPOSED STANDARDS

Supporting Information. In developing the standards proposed herein the Administrator has given careful consideration to each of the factors enumerated in section 307(a)(2). These factors include ". . . the toxicity of the pollutant, its persistence, degradability, the usual or potential presence of the affected organisms in any waters, the importance of the affected organisms and the nature and extent of the effect of the toxic pollutant on such organisms." In light of the Act's manifest concern for public health, which is reflected in both the statute and the legislative history, the Administrator has also considered available data concerning human health effects attributable to benzidine. The data considered by the Administrator relating to these factors of toxicity and environmental fate and effect are set forth in a Benzidine Criteria Document. The Criteria Document, together with the general introduction to that document, are hereby incorporated by reference as a part of the statement of basis and purpose for the standards hereinafter proposed.

In addition, the Administrator has considered information with respect to present discharge levels and the availability of various methods of control and related technology by which discharge of benzidine might be eliminated or reduced. His authority to consider technology as well as economic impact is discussed in detail in the preamble portion of the Notice of Proposed Toxic Pollutant Effluent Standards published on June 10, 1976, noted previously. In order to obtain relevant data for this function, EPA engaged the services of an outside consultant, Thomas M. Keinath, Ph.D., who is a recognized expert on wastewater treatment technology. Dr. Keinath has prepared and submitted a report to the Agency describing the benzidine manufacturing and benzidine-based dye applicator industries, and examining control technologies which are actually in use or which are or may be available to the industries for whom coverage is proposed under this rulemaking. His report is hereby incorporated by reference as a part of the statement of basis and purpose of the standards herein proposed.

The Agency has also evaluated the economic impact of implementing the technologies identified for achieving the effluent standards for benzidine-based dye manufacturers and users. Since there will be no direct discharges from manufacturers no substantial economic impact is anticipated for that subcategory.

The Agency recognizes that the effluent standard for dye applicators may create a cost burden for monitoring, particularly for the small benzidine-based dye applicator, if compliance cannot be shown by the mass balance approach. Therefore, the Agency solicits public comment and information on defining such cost burdens. The Agency further recognizes that the effluent standard for benzidine-based dye applicators which are new sources may be difficult to meet during the initial plant start-up period. Public comments and information are also solicited on this point.

Copies of the aforesaid criteria document, technology assessment report and supporting materials are available for public inspection and copying at the U.S. Environmental Protection Agency, Public Information Reference Unit, Room 2922, (EPA Library), 401 M Street, S.W., Washington, D.C. 20460 during normal business hours. In addition, copies of the criteria document and technology assessment report may be inspected and copied at similar public information reference units in each of the ten EPA Regional Offices, and may be purchased from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia.

Development of the Standards. The general approach used in deriving the proposed benzidine standards is consistent with that used for the previously proposed pesticide effluent standards (see 41 FR 23576). However, application of that approach has resulted in a primary emphasis on protection of human health in light of the known carcinogenicity of benzidine to humans. As noted in the preamble accompanying the promulgation of benzidine as a § 307(a) toxic pollutant, benzidine was included because, "the resulting potential for increased water pollution by this known carcinogen and the adverse effects on the environment which may result, require the listing of benzidine." (38 FR 24343).

Although benzidine exhibits acute toxicity to fish at concentrations in the order of 2 to 10 milligrams per liter (mg/l) and has exhibited bioaccumulation of more than 40 times in fish, current usage and in-place control systems prevent detectable concentrations (normally 0.2 μg/l or greater) of benzidine from occurring in receiving waters. Available studies also indicate that benzidine in low concentrations (in the range of about 50 μg/l or less) disappears from the water column. Because benzidine is rarely if ever discharged in concentrations which approach the levels of acute toxicity to aquatic organisms, and does not appear to be persistent, it is not presently believed to pose a significant threat to aquatic life. The Agency's principal concern with benzidine, therefore, is its potential carcinogenic effects on humans.

GENERAL PROVISIONS

The Notice of Proposed Rulemaking published on June 10, 1976, proposed provisions of general applicability to all standards issued under section 307(a). These were set forth as §§ 129.1 through 129.8. Those Sections as promulgated will be applicable to standards established hereunder for benzidine. Owners and operators of facilities which are or may be subject to the standards proposed herein are expressly referred to that notice of proposed rulemaking for provisions relating to scope and purpose, definitions, abbreviations, compliance procedures (including notification of the Regional Administrator or State Director of an approved NPDES permit program, as appropriate, of any discharge subject to these standards), requirements and procedures for estamlishment of a more stringent effluent limitation than that prescribed in the standards established in these proceedings, and compliance date.

In the Notice of Proposed Toxic Pollutant Effluent Standards published on June 10, 1976, standards were proposed for aldrin/dieldrin, DDT (DDD, DDE), endrin, and toxaphene in §§ 129.100 through 129.103, respectively. The present proposal would add a new § 129.104 containing the effluent standards for benzidine.

The standards proposed in the new § 129.104 provide coverage for new and existing sources in the following industrial categories: manufacturers of benzidine and benzidine-based dyes; manufacturers of paper goods who use any benzidine-based dye in any product or process; manufacturers of leather goods who use any benzidine-based dye in any product or process; and manufacturers of textile goods who use any benzidine-based dye in any product or process. For purposes of these standards, a new source is defined as any source on which construction is begun following the date of proposal of effluent standards, if effluent standards are subsequently promulgated. For purposes of the standards proposed at this time, the determinative date with respect to new sources is the date of this publication.

Each section includes specialized definitions of the point source category covered and prescribe acceptable analytical methods. In addition, provision is made for determination of weights and concentrations. The specific factors considered by the Agency in developing the numerical standards are discussed in the following paragraphs.

(1) *Dye Manufacturing and Dye Applicators; Wastewater Characteristics.* The manufacture of benzidine-based dye is a two-step operation. The first step is the manufacture of benzidine, which is formed from hydrazobenzene. The hydrazobenzene is rearranged to a benzidine salt by the addition of acid. In the second step, which is a separate process, the benzidine salt is subjected to a tetrazotization reaction and is then susceptible for reaction with various chemicals to form the individual dyes. In general, the benzidine salt production and the benzidine-based dye production are performed in separate buildings because of the strict OSHA regulations promulgated for benzidine production facilities.

Each of the three present manufacturers performs both of these steps, and therefore is both a benzidine manufacturer and a benzidine-based dye manufacturer. Benzidine itself is thus manufactured only as an intermediate product in the dye manufacturing process.

The sources of wastewaters in the benzidine manufacturing operation include wash waters from reaction vessels and filters (where used), air pollution scrubber blowdown, worker laundry and shower wastes, and floor washdown waters. These wastes are collected in batch reactor vessels at Allied and GAF for subsequent treatment. These wastes are discharged without any pretreatment at Fabricolor.

Wastewater volumes for the three benzidine-based dye manufacturers have been reported by the Synthetic Organic Chemicals Manufacturers Association (SOCMA) for the benzidine manufacturing portion of the dye making process. It was estimated that Allied Chemical produces 2.64 million gallons of wastewater per year during the manufacture of 1 million pounds of benzidine. The concentration of benzidine in the untreated wastewater has not been determined analytically. GAF produces approximately 78,000 gallons of wastewater per year while manufacturing 140,000 pounds of benzidine. The concentration of benzidine in their raw wastewater has likewise not been determined. Fabricolor produces 760,000 gallons of wastewater per year while manufacturing 60,000 pounds of benzidine. The concentration of benzidine in untreated wastewater from the entire plant (including dye production) has been calculated to be approximately 10 μg/l.

The benzidine-based dye production wastes include the so-called "mother liquor," which is the waste product following the dye extraction and the typical wash waters from equipment and operating areas. The benzidine concentrations in these wastewaters are generally less than the 10μg/l analytical sensitivity using the conventional chloramine T detection method, but occasionally have been found to exceed 100 μg/l based on available analytical results. Both Allied Chemical and GAF mix these wastes with the treated benzidine wastes, and provide some flow equalization and pH adjustment before final disposal.

Benzidine-based dye applicators pose substantially different problems. Dye-related wastewaters do not constitute a large fraction of oxygen demanding wastes in textile, paper or leather plants. Such dye wastes do pose aesthetic problems in receiving waters and under certain conditions may contribute to acute toxicity. A complete description of wastewater characteristics for those industries is available in the "Development Documents" published by EPA in connection with the development of effluent limitations guidelines and new source performance standards for each of those industries under sections 301, 304, and 306 of the Act.

Benzidine concentrations in benzidine-based dye applicator wastewaters can be based on a so-called "mass balance monitoring approach." The mass balance monitoring approach is premised on the dye applicator noting the use of a benzidine-based dye and the accompanying water usage. The operator determines the total volume of waste discharged during the operating day. The concentration is calculated by dividing the maximum amount of benzidine potentially present (provided on the manufacturers label) by the total volume of water used during the working day. This method is justified because typically the facilities providing treatment have hydraulic detention times in excess of an operating day. The facilities thus act as equalization basins and dampen concentration variations. In comparisons with actual analytical results, the concentration calculated by the mass balance approach invariably yielded conservative estimates (i.e. higher than the analytical result).

In the textile plant surveyed as a model in connection with the development of this regulation, calculations which were made assuming undiminished benzidine concentrations in spent dyes indicated median benzidine concentrations of 13.07 μg/l with a calculated maximum daily concentration as high as 17.7 μg/l. Actual measured concentrations by chemical analyses measured on a subsequent operating day averaged 3.5 μg/l. A questionnaire survey of 3 other textile plants which use benzidine-based dyes but as a lower percentage of the total dyes used, indicated average calculated concentrations of 0.25, 0.15 and 0.41 μg/l, respectively, in their effluents although one plant had one day with a calculated benzidine concentration of 3.2 μg/l.

In the leather tanning plant surveyed as a model in connection with the development of this regulation, calculations which were made assuming undiminished benzidine concentrations in spent dyes indicated a dye house blowdown wastewater concentration of 0.38 μg/l. Other plant wastes diluted the benzidine concentration to 0.25 μg/l before introduction into the waste treatment facility. Two other facilities surveyed by questionnaire had calculated average benzidine concentrations of 0.73 μg/ and 0.27 μg/l, respectively.

In the paper dyeing plant surveyed as a model in connection with the development of this regulation, calculations which were made assuming undiminished benzidine concentrations in spent dyes indicated that the concentration in the exhausted pulping liquors averaged 4.5 μg/l with a maximum daily benzidine concentration calculated to be 8.5 μg/l. Four other facilities surveyed by questionnaire had calculated average benzidine concentrations of 0.02, 0.49, 0.004 and 3.2 μg/l, respectively, in their effluents.

Available data, therefore, indicate that all three of the principal applicator categories had benzidine concentrations which were normally less than the 10 μg/l average daily concentration proposed in these standards. However, the calculated maximum daily concentrations are significant. A dye applicator typically varies the type of dye used and may use a higher percentage of benzidine-based dye than reflected in these data during a particular period of time. Therefore, the calculated discharge concentrations might be substantially higher than reflected here. Furthermore, the sample size reported here is small and it is believed that the concentrations in the effluents from other plants in each of these categories may not be as low as those reported above. To provide additional data regarding the discharge of benzidine by dye applicators, the Benzidine Task Force of SOCMA conducted an analytical survey of the wastewaters of representative plants for each of the 3 industrial subcategories. None of the samples showed concentrations at the chloramine T detection limit of 10 μg/l benzidine. These results are consistent with mass balance calculations reported above which were made on similar effluents.

One potential problem remains concerning discharge by benzidine-based dye users. If strong reducing conditions exist, benzidine based dyes conceivably can be reduced to the parent compound, benzidine. Such reducing conditions can occur if the reductive stripping of dyes from product materials failing to meet quality control standards is practiced, or if reductive materials are used elsewhere in the manufacturing process and become mixed with benzidine-based dyes in the sewers or waste treatment system. Oxidative stripping can be used rather than reductive stripping which can eliminate that possibility. However, no data are available to demonstrate the occurrence of dye reduction to benzidine under the reducing conditions prevalent in these industrial discharges. The limited sampling and chemical analyses of such effluents have not shown any unexpectedly high concentrations of benzidine and therefore the Agency has no information indicating that such benzidine formation is in fact taking place.

(2) *Toxicity.* Benzidine has not been studied extensively for toxicity to aquatic species since the main concern has been its carcinogenic activity in man. However, initial 96-hour TL50 values from static bioassays with benzidine have ranged from 2.5 mg/l for the red shiner, to 20 mg/l for one test for the fathead minnow.

(3) *Human Health Effects.* The incidence of bladder tumors resulting from occupational exposure to aromatic amines was first described by Rehn in Germany in 1895. Long-term retrospective studies undertaken in workers exposed to dyes and dye intermediates have associated the manufacture of benzidine with a high risk of developing bladder cancer. Average latency periods from first exposure to detection of the first tumor is 17 years. It has been noted that trying to decrease the potential exposure by limiting the duration of employment on the process only serves to increase the number at risk.

Accordingly, the Occupational Safety and Health Administration (OSHA) of the United States Department of Labor

has established benzidine standards prescribing procedures and requirements to minimize human contact in the work place, applicable to any area in which benzidine is manufactured, processed, repackaged, released, handled or stored. These stafety standards are set forth at 29 CFR 1910.1010.

The Agency does not have any evidence at this time of actual, direct exposure of humans to benzidine in the aquatic environment or through ingestion from drinking water sources.

(4) *Persistence; Degradability.* Benzidine has been detected in the Sumida River in Tokyo, Japan, at concentrations up to 233 μg/l though it has not been found in navigable waters of the United States. To date, through the limited studies conducted, benzidine has been shown to be inhibitory to bio-oxidation by activated sludges during sewage treatment at a concentration of 500 mg/l, slightly inhibitory at a concentration of 1–5 mg/l, and thought to be bio-oxidized at a concentration of 0.1 mg/l or less. Benzidine disappears from the water column following discharge, and therefore is not regarded as persistent.

(5) *Bioaccumulation.* Through a radiometric analysis, bluegills have been shown to bioconcentrate residues from 14C-benzidine to a factor of 44 times the water concentration in the edible portions of the fish.

(6) *Criteria Formulation.* Benzidine has not been studied extensively for toxicity to aquatic species since the main concern has been its carcinogenic activity in man. Bioassays with benzidine have produced 96-hour TLms as low as 2 mg/l for fish. The bioaccumulation study referenced above showed that edible tissue residues can accumulate up to 44 times the ambient water level.

Because neither epidemiological nor other human dose-response data exist, an ambient water quality level protective of human health for benzidine has been calculated based in part upon mathematical extrapolation modelling. The extrapolation is set forth in Appendix 1 to the Benzidine Criteria Document. The results of that approach, as well as the qualifications inherent in the use of those results, are summarized as follows. Levels of benzidine which produce a lifetime risk of no more than one tumor per million people exposed, if allowed to reach man through water, are estimated to range from 0.05 μg/l to 0.8 μg/l depending on the data and extrapolitan method employed. Calculations based upon risks of one tumor per 500,000 people exposed, or 10 million exposed, do not result in a substantial expansion of the magnitude of this range. These extrapolation methods for estimating human dose response from animal data are inherently imprecise. They are used solely to furnish some indication of relationship between exposure levels and potential risks. Such methods must be used carefully and in coordination with all other data available in establishing protective criteria. Moreever the figures are likely to be over protective because the extrapolation assumes a continuing lifetime exposure to two liters of water containing the calculated benzidine concentration daily. Accordingly, their use here should not be construed as a general statement of Agency policy regarding acceptable levels of risks or as a percent for regulating action by the Agency in other contexts.

Benzidine does not persist in the water column following discharge, and to date has not been detected in the aquatic environment of the United States. For this reason as well as all of the reasons set forth in the preceding paragraph, the Agency does not believe that setting a criterion at the lower level (0.05 μg/l) indicated by the mathematical modelling is justified. Considering the general range indicated by the modelling and the lack of evidence of actual direct human exposure from water, an ambient water criterion of 0.1 μg/l is recommended. Presently available data indicate that an ambient water criterion at this level will provide the requisite degree of safety for human health as well as for aquatic organisms, consistent with the statutory purposes of section 307(a).

(7) *Control Technology Available to Manufacturers and Dye Applicators.*

BENZIDINE MANUFACTURING WASTEWATERS

Because benzidine is a recognized carcinogen, plant operating procedures in its manufacture are designed to contain wastes in closed vessels to the maximum extent feasible in order to protect personnel. Waste treatment, as currently practiced by Allied Chemical Co. and GAF, is by the so-called nitrous acid oxidation procedure. The treatment is provided on a batch basis. In essence, all of the benezidine-related wastes are placed into a reactor vessel where a sodium nitrite solution is added along with a strong acid (either sulfuric or muriatic) to lower the pH to 2.0. The temperature is reduced to 10 C. The nitrite solution is added until the presence of excess nitrite is detected in the reactor vessel. Following this treatment, the wastes are released for mixing with other plant wastes and ultimate introduction into a reciving POTW system.

Other systems have been investigated for these concentrated wastewaters. Activated carbon adsorption technology is capable of reducing concentrations to the 1–10 μg/l level. This technology has not been demonstrated on a full scale system for benezidine wastes and could require up to 2 years for implementation. Preliminary cost figures based on projections from laboratory data appear to be one-third to one-half that for the nitrous acid procedure. Industry has expressed a reservation with regard to the use of activated carbon because of the possibility of increased worker exposure to benzidine sorbed on the carbon. However, currently available carbon handling systems minimize worker contact to less than present OSHA requirements.

Ozone treatment has also been evaluated. An experimental ozonation system has been shown to reduce benzidine from 117 mg/l to 0.01 mg/l in 36 minutes. However, a capital expenditure of several million dollars has been estimated for the entire industry which from an economic viewpoint is non-competitive with other potential systems.

Other systems evaluated included polymeric adsorbents and direct radiation. However, insufficient data were available to project the feasibility of these systems.

In addition to physical-chemical systems described above, an evaluation of the effects of benzidine on bio-oxidation systems has also been made. Available data indicate that benzidine is toxic at concentrations of 500 mg/l, is slightly inhibitory at concentrations of 1 to 5 mg/l and is non-toxic to such systems at 0.1 mg/l. More recent laboratory studies with acclimated activated sludge-type biological systems have indicated that benzidine is biodegradable at a 0.045 mg/l concentration with 90 percent undergoing degradation and 10 percent being incorporated into the activated sludge mass. Thus, biological treatment systems apparently will effectively treat diluted nitrous acid wastes from manufacturers.

BENZIDINE-BASED DYE MANUFACTURING WASTEWATERS

Wastewaters from the manfacturers contain benzidine concentrations of approximately 100 μg/l in the highly colored "mother liquor." At present at both Allied Chemical and GAF, these are mixed with the treated benzidine wastewaters and are subjected to flow equalization and pH adjustment before discharge. Each of the three present manufacturers either discharges to a municipal POTW or, in the case of GAF, plans to do so as soon as such facilities are available. Information available to EPA indicates that the benzidine levels discharged would not inhibit biological secondary treatment systems and that such systems would achieve significant removals.

BENZIDINE-BASED DYE APPLICATOR (USER) WASTEWATERS

The typical waste treatment systems applied to these wastewaters are either the aerated lagoon or extended aeration variations of the activated sludge biological treatment process. Such processes are consistent with the 1977 requirements under the Act, although such treatment is not necessarily required in order to meet the standards hereinafter proposed. Because existing controls appear capable of meeting the proposed standards, no other system has been evaluated for dye applicators in connection with this rulemaking. The wastes from these facilities contain only small quantities of benzidine and should receive adequate treatment from such biological treatment installations as installed either at the industrial site or by municipal systems employing similar biological treatment systems.

(8) *Economic Impact.* The economic impact of the proposed regulations on the direct dischargers of benzidine is expected to be insignificant. Following the connection of GAF to the Rensselaer, NY, POTW, there will be no existing benzidine dye manufacturers who dis-

charge directly. Although the likelihood of new manufacturing sources of benzidine or benzidine-based dyes appears small, such an operator could use activated carbon adsorption treatment for concentrated benzidine manufacturing wastes. Costs for this technology appear to be less than the nitrous acid treatment systems in current use. Costs for carbon adsorption treatment could be passed through to subsequent users since the benzidine-based dye market price already reflects similar or even higher treatment costs for the nitrous acid process now used by the major producers.

For dye applicators in the textile, leather and paper products subcategories, the cost of compliance with the proposed mass balance monitoring approach will be restricted to only a very small additional administrative cost for recordkeeping and reporting, except in those cases where compliance with the standards would require use of the 40 CFR 136 procedure. In such cases, significant costs could result and the Agency solicits information on such costs and impacts.

(9) *Rationale for Standards.* The general approach taken by the Agency in developing the proposed standards for benzidine has been mentioned above. For the reasons previously set forth, the recommended ambient water criterion for benzidine which is protective of both aquatic life and human health is 0.1 μg/l.

In developing the proposed standards for benzidine, the Agency has considered not only the risks of exposure which are reflected in the recommended ambient water criterion, but also its behavior in the aquatic environment following discharge. As recognized in the preamble to the Notice of Proposed Toxic Pollutant Effluent Standards published on June 10, 1976, "translating a safe water quality criterion number to an end-of-the-pipe standard is at best an imprecise calculation." In addition to benzidine's apparent lack of persistence in the water column, the actual discharge concentration of any substance from a point source does not normally remain the ambient concentration. In fact, for the typical discharge situation, the effluent disperses following discharge and becomes greatly diluted. The area of dilution is often referred to as a "mixing zone," and will vary in size and shape from one body of water to the next. The result of this phenomenon is that the pollutant concentration typically becomes greatly diluted in the receiving water and may not even be detectable.

In most cases, therefore, an effluent standard which includes a concentration of the pollutant which is considerably greater than that desired in the ambient water will nevertheless result in achievement of the concentration reflected in the ambient water criterion at the edge of and beyond a reasonable mixing zone. To deal with situations where the receiving water conditions provide insufficient dispersion and dilution, or a water use exists in such close proximity to a discharge that removal through natural processes is insufficient to provide the ample margin of safety required by the Act, a mechanism in the nature of a "tightening variance" clause was proposed in § 129.7 of the rulemaking proposed on June 10, 1976. This variance would allow establishment of a more stringent limitation on effluents where the particular characteristics of the local receiving waters so warrant.

The calculation of effluent standards for benzidine and benzidine-based dye takes into account the two operations described above, i.e. production of the benzidine and production of the dyes. In the benzidine manufacturing operation, the concentrated benzidine manufacturing wastes are treated by the nitrous acid oxidation procedure. Available information indicates that benzidine concentrations of less than 10 μg/l are achievable on the average with this process. This provides the basis for calculating a maximum average daily concentration in the effluents.

A limitation on the weight of benzidine discharged per unit of production is specified in order to prevent a manufacturer from discharging larger quantities of benzidine to the environment than necessary, and then using dilution alone to comply with the standards. GAF's estimated annual production of 140,000 pounds of benzidine with the annual discharge of 78,000 gallons of wastewater at a benzidine concentration of 10 μg/l, results in a mass emission limit of 0.00005 kg benzidine per 1000 kg of benzidine produced.

The second component of the operation, namely the actual dyestuff manufacture, must be added to the benzidine contributed by the benzidine manufacturing process. GAF has reported that the sampling point which contains the dye manufacturing wastes averages 600,000 gallons per day. Using an achievable concentration of 10 μg/l, the mass emission can be calculated as 0.050 pounds per day (0.0227 kg per day). Utilizing the estimated 140,000 pounds per year of benzidine produced by GAF and an estimated 360 operating days per year, the mass emission rate from this operation is calculated to be 0.1288 kg benzidine per 1000 kg of benzidine produced. Addition of the benzidine mass loading from the benzidine manufacturing operation with that from the dye manufacturing operation yields a mass loading of approximately 0.130 kg benzidine per 1000 kg of benzidine produced. This is proposed as the maximum average daily loading standard for manufacturers.

Insufficient data are available to characterize the benzidine concentration variations in combined wastewaters with statistical precision. For example, GAF has sampled wastes principally composed of dye manufacturing wastes. Of the 52 daily composite samples collected at this sampling point, 45 had benzidine concentrations less than the 5 μg/l detection limit inherent in their sampling methods. Seven samples had concentrations ranging as high as 134 μg/l with three samples (5.8 percent) exceeding 50 μg/l.

Because these processes are batch processes, the manufacturers have control over times of release. Therefore, a variability factor of five multiplied by the average concentration is reasonable for this industry as a maximum permissible concentration for any day. Thus the data available to the Agency indicate that existing sources in the manufacturing subcategory can achieve an effluent standard of a daily average computed from the results over a calender month of 10 μg/l and not to exceed 50 μg/l for the results representing any working day. Considering the disappearance of benzidine from the water column after discharge, the absence of high bioaccumulation rates, and the existence of normal dilution and dispersion factors, discharges at the aforesaid levels would appear to avoid concentrations in ambient receiving waters in excess of 0.1 μg/l. Therefore, thees levels are proposed by the Agency for existing manufacturing sources.

With respect to applicators, plants in this category, based upon the available data, can achieve an effluent concentration of 10 μg/l of benzidine, as calculated by the mass balance monitoring approach, as a daily average by the use of in-place technology. The Agency believes that the actual concentration as determined by the method specified in 40 CFR 136 (chloramine T) is actually substantially lower. This in-place technology typically includes either extended aeration or aerated lagoons which have hydraulic detention times exceeding one working day and possibly several days. These tanks or basins provide mixing and dampen concentration variations of influent wastewaters. In addition, applicators can carefully manage the scheduling of benzidine use and the subsequent release of dye baths to avoid excessive concentrations. This technique can assist in complying with the standard, and further reduce variability in the concentrations from day to day. For these reasons, the use of a variability factor of only 2.5 times the average for the maximum allowable concentration is justified. Accordingly a maximum allowable concentration for any working day of 25 μg/l is proposed for the applicators. Because the amounts of benzidine in the wastes of the applicators are inherently quite small, no weight loading limitation is proposed for these categories.

Because standards proposed for existing manufacturing and applicator sources appear to provide the requisite protection based upon presently available data, the proposed standards for new sources are the same as for existing sources.

As these industries achieve the 1977 effluent limitations required under sections 301, 304, and 402 of the Act, benzidine concentrations in actual practice may be further reduced. In addition, subsequent monitoring or other information may require a later revision of these standards in the direction of greater stringency. C.f. section 307(a)(3). How-

ever, based on existing information the standards proposed at this time would appear to provide that degree of safety and protection required by section 307(a) of the Act.

III. Public Participation in Rulemaking Process

A public hearing to consider the proposed effluent standards will be held pursuant to section 307(a)(2) of the Act commencing on July 30, 1976, at 10:00 AM in Room 2409, Waterside Mall, EPA, 401 M Street, S.W., Washington, D.C. In accordance with the Agency's rules of practice governing public hearings on effluent standards for toxic pollutants, 40 CFR Part 104 as amended, 41 FR 17898 (April 29, 1976), the first hearing day will include a prehearing conference at the above stated time and place. All persons interested in participating in those hearings as objecting parties should refer to the amended rules of practice, 41 FR 17898, and should not rely on previous editions. Any person who has objection to any standard proposed herein may file with the Hearing Clerk (A-100), Room 1019 WSME, U.S. Environmental Protection Agency, 401 M Street, SW., Washington, D.C. 20460, within 25 days of the date of this notice, a statement of objection in triplicate which shall meet all of the requirements of 40 CFR 104.3 (a) and (b). The presiding officer may refuse to permit any person to participate in said hearing who fails to comply with any of the provisions of those sections.

In addition to the foregoing, any person interested in this proposed rulemaking but who does not participate as a party in the formal hearing may submit written comments to the Agency on the proposed rulemaking. Such comments should be filed in triplicate, if possible, and should be addressed to: Hearing Clerk (A-100), Room 1019 WSME, U.S. Environmental Protection Agency, 401 M Street, SW., Washington, D.C. 20460. All comments which are received by the hearing clerk and which are postmarked on or before July 30, 1976, shall become a part of the hearing record in the manner prescribed in 40 CFR 104.3(d) and shall be considered by the Administrator prior to the promulgation of final standards.

Dated: Jun 21, 1976.

Russell E. Train,
Administrator.

1. In 40 CFR Part 129, Subpart A (as proposed at 41 FR 23576 (June 10, 1976)), is amended by adding a new entry to the table of contents to read as follows:

Sec.
129.104 Benzidine.

§ 129.4 [Amended]

2. Subpart A of Part 129 is further amended by adding new paragraph (e) to § 129.4 to read as follows:

(e) Benzidine—"Benzidine" means the compound benzidine and its salts as identified by the chemical name 4,4'-diaminobiphenyl.

3. Subpart A of Part 129 is further amended by adding new § 129.104 to read as follows:

§ 29.104 Benzidine.

(a) *Specialized definitions.* (1) "Benzidine Manufacturer" means a manufacturer who produces benzidine or who produces benzidine as an intermediate product in the manufacture of dyes commonly used for textile, leather and paper dyeing.

(2) "Benzidine-Based Dye Applicator" means an owner or operator who uses benzidine-based dyes in the dyeing of textiles, leather or paper.

(3) The ambient water criterion for benzidine in navigable waters is 0.1 μg/l.

(b) *Benzidine manufacturer*—(1) *Applicability.* (i) These standard apply to:

(A) All discharges into the navigable waters of process wastes; and

(B) All discharges into the navigable waters of wastes containing benzidine from the manufacturing areas, loading and unloading areas, storage areas, and other areas subject to direct contamination by benzidine or benzidine-containing product as a result of the manufacturing process, including but not limited to:

(*1*) Stormwater and other runoff, and

(*2*) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of benzidine; or to stormwater runoff that exceeds that from the ten year 24-hour rainfall event.

(2) *Analytical method acceptable.* Environmental Protection Agency method specified in 40 CFR Part 136.

(3) *Effluent standards*—(i) *Existing sources.* Discharges from a benzidine manufacturer shall not contain benzidine concentrations exceeding an average per working day of 10 μg/l calculated over any calendar month, and shall not exceed a monthly average daily loading of 0.130 kg/kkg of benzidine produced, and shall not exceed 50 μg/l in a sample(s) representing any working day.

(ii) *New sources.*—Discharges from a benzidine manufacturer shall not contain benzidine concentrations exceeding an average per working day of 10 μg/l calculated over any calendar month, and shall not exceed a monthly average daily loading of 0.130 kg/kkg of benzidine produced, and shall not exceed 50 μg/l in a sample(s) representing any working day.

(4) The standards set forth in this paragraph (b) shall apply to the total combined weight or concentration of benzidine, excluding any associated element or compound.

(c) *Benzidine-based dye applicators*—(1) *Applicability.* (i) These standards apply to:

(A) All discharges into the navigable waters of process wastes; and

(B) All discharges into the navigable waters of wastes containing benzidine from the manufacturing areas, loading and unloading areas, storage areas, and other areas subject to direct contamination by benzidine or benzidine-containing product as a result of the manufacturing process, including but not limited to:

(*1*) Stormwater and other runoff, and

(*2*) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of benzidine; or to stormwater that exceeds that from the ten year 24-hour rainfall event.

(2) *Analytical method acceptable.* (i) Environmental Protection Agency method specified in 40 CFR Part 136; or

(ii) Mass balance monitoring approach which requires the calculation of the benzidine concentration by dividing the total benzidine contained in dyes used during a working day (as certified on the label by the manufacturer) by the total quantity of water discharged during the working day.

[Note.—The Regional Administrator (or State Director, if appropriate) may rely entirely upon the method specified in 40 CFR Part 136 in analyses performed by him for enforcement purposes.]

(3) *Effluent Standards*—(i) *Existing Sources.* Discharges from benzidine-based dye applicators shall not contain benzidine concentrations exceeding an average per working day of 10 μg/l calculated over any calendar month; and shall not exceed 25 μg/l in a sample(s) or calculation(s) representing any working day.

(ii) *New Sources.* Discharges from benzidine-based dye applicators shall not contain benzidine concentrations exceeding an average per working day of 10 μg/l calculated over any calendar month; and shall not exceed 25 μg/l in a sample(s) or calculations(s) representing any working day.

(4) The standards set forth in this paragraph (c) shall apply to the total combined concentrations of benzidine, excluding any associated element or compound.

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